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(54) Title: SOLVENTLESS POLYURETHANE SPRAY COMPOSITIONS AND METHOD FOR APPLYING THEM

(57) Abstract

A method for preparing polyurethane by spraying solventless, equal volume mixtures of: (a) a liquid polyisocyanate; polyisocyanurate or isocyanate terminated quasi-prepolymer; and (b) a curing agent comprised of a blend of from about 0 to 15 % of a polyamine having an equivalent weight from about 30 to about 200, about 10 to 20 % of a low molecular weight glycol having an equivalent weight of from about 30 to 200, about 40 to 80 % of a relatively high molecular weight polyol or polyamine having an equivalent weight of about 350 to 2000, and about 1 to 20 % of a synthetic zeolite molecular sieve, wherein the average equivalent weight of (b) is from about 150 to 500.

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10 SOLVENTLESS POLYURETHANE SPRAY COMPOSITIONS AND
METHOD FOR APPLYING THEMField of the Invention

15 This invention pertains to two-component solventless spray compositions for producing polyurethane and poly(urea)urethane coatings, the products produced from these compositions, a process for producing such products, and methods for using them.

Background of the Invention

20 Polyurethane coatings are well known and have gained commercial acceptance as protective and decorative coatings for metal, wood, concrete, foam, and plastics in the aircraft, construction, product-finishing, textile and maintenance/architectural coatings markets. The 25 basic raw materials used to prepare these coatings generally comprise as essential components (a) an aliphatic or aromatic di-or-polyisocyanate and (b) a co-reactant or curative component bearing active hydrogen containing groups, i.e., hydroxyl or amine groups, or 30 latent active hydrogen containing groups, e.g., oxazolidines or ketimines. For typical two-package coating systems, the co-reactant is usually a hydroxyl group containing oligomer chosen from the general classes of polyesters, polyethers, alkyd resins and acrylics.

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1 The co-reactant component is generally the vehicle for
pigment (grinding) and may also contain other additives
such as catalysts, plasticizers, bitumenous extenders,
suspending agents, anti-skimming agents, surfactants, and
rheological modifiers.

5 Both the isocyanate-containing component and the
active hydrogen-containing co-reactant usually contain
volatile organic solvents whose primary function is to
lower viscosity thereby providing a consistency suitable
10 for spray application with conventional air, airless and
electrostatic spray equipment.

15 A growing emphasis on compliance with government
environmental and health hazard regulations that limit
both the type and amount of volatile organic compounds
(VOC) has prompted coating manufacturers and end users to
evaluate new coating technologies.

20 Prior art high solids and solventless polyurethane
coatings have been developed which comply with solvent
emission regulations. As used herein, a solventless
polyurethane coating is one in which substantially all of
the constituents remain in the applied coating.

25 The first solventless, urethane coatings were the
"one shot" systems, so named because no prereaction of
components is involved. Typical "one shot" systems
consist of a pure isocyanate component, usually
4,4'-diphenylmethane diisocyanate (MDI), and a curative
component comprised of a blend of active hydrogen
containing co-reactants, for example polyether or
polyester polyols and lower MW glycol, with fillers and
catalyst. The components are usually combined at
30 volumetric mix ratios of 1:1 to 4:1. Although coating
systems of this type are sprayable without the use of a
solvent, there are some disadvantages. One shot systems
are moisture sensitive because they contain a very high
percentage of unreacted diisocyanate, usually 26-31% by
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1 weight, and cannot be sprayed under humid conditions
without blowing or foaming. Another major disadvantage
of one shot spray systems is reflected in the low
physical properties of the polyurethanes they produce.
5 Important physical properties such as tensile and tear
strength and abrasion resistance are inferior to those
obtained by solvent containing systems.

Prior art two package, solventless polyurethane
coating systems with superior physical properties have
10 also been developed. These spray systems are generally
based on an isocyanate-containing prepolymer component
combined with a curative component comprised of a
viscous, sometimes solid, polyamine whose viscosity has
been reduced by addition of a non-volatile diluent or
15 whose volume has been adjusted with "polyol" so that it
can be combined with the isocyanate component at
predetermined volumetric mix ratios.

U.S. Patent 4,195,148 and U.S. Patent 4,234,445
disclose solventless polyurethane coatings which use a
20 non-reactive, non-volatile lactone viscosity modifier to
dissolve viscous or solid prepolymer and curative
components to reduce viscosity of the systems so that
they may be applied using airless, plural-component spray
equipment.

U.S. Patent 4,267,299 also discloses sprayable,
25 solventless polyurethane compositions which combine an
isocyanate terminated prepolymer component (Part A) with
a curative component (Part B). The curative component is
a blend of highly reactive polyamine with a slower
reacting, higher molecular weight (MW) polyol. Part B
30 includes enough highly reactive polyamine to react with
substantially all of the isocyanate groups in the Part A
within 2 to 5 minutes. The higher MW polyol is present
in relatively small amounts and functions as a "reactive
filler" or bulking agent which allows the Part A and Part
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1 B to be combined in ratios of from 2:1 to 4:1.

5 The polyurethane produced from preferred embodiments
of prepolymer-based, prior-art inventions (U.S.
4,195,148, U.S. 4,234,445 and U.S. 4,267,299) have
superior physical properties such as tensile strength,
tear strength, and abrasion resistance compared to
one-shot, solventless coating systems. Moreover, such
10 prepolymer-based solventless coating systems are
generally less sensitive to moisture than one-shot
solventless systems because pre-reaction of the
isocyanate with polyol to form the prepolymer component
results in less reactive isocyanate, typically 3 to 12%
by weight.

15 There are some disadvantages associated with prior
art, prepolymer based solventless polyurethane coatings.
For optimum mixing, a ratio of 1:1 is desirable;
preferred embodiments of the prior art have volumetric
mix ratios of 3:1. A major disadvantage of preferred
embodiments of prior-art, prepolymer-based, solventless,
20 polyurethane coatings is that the components must be
heated to 160°F - 200°F to reduce viscosities for spray
application. Heating, maintaining and applying
components at 160 - 200°F requires additional equipment
such as drum heaters to warm viscous materials to a
pumpable viscosity, electrical induction heaters to
25 further raise component temperatures and reduce
viscosity, and the use of heated hoses to maintain
temperature until the components enter the spray gun.
Prior-art systems have fast gel times, typically 0.5 to 3
30 minutes at application temperatures of 160 - 200°F, and
must be applied with an internal mix, plural-component
spray gun such as the Binks 43-P. Internal mix spray
guns of this type are connected to three spray hoses; one
for each component and one for solvent flushing. The
hoses increase the weight of the spray gun, make the gun
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1 awkward to use, and severely restrict the movement of the
 applicator in confined areas such as manholes or covered
 hopper cars. Accordingly, a solventless, polyurethane
 coating composition is needed which combines the ease of
5 application at ambient temperatures and superior physical
 properties.

Summary of the Invention

10 The two component, solventless spray composition for
 producing polyurethane and poly(urea)urethane coatings of
 the present invention includes substantially equal
 volumes of an isocyanate-containing component and a
 curative component. The isocyanate-containing component
 comprises a liquid polyisocyanate, polyisocyanurate or
15 isocyanate-terminated prepolymer or quasi-prepolymer.
 The curative component is comprised of from about 0% to
 about 15% by weight of one or more polyamines
 (di-or-polyamines) or alkanolamines in an amount
 sufficient to react to form a thixotropic mixture about
20 15 seconds to about 2 minutes after being mixed with the
 isocyanate-containing component, from about 10% to about
 20% by weight of one or more glycols having an equivalent
 weight in the range from about 30 to about 200, from
 about 40% to about 80% by weight of one or more high
25 molecular weight polyols or polyamines having an
 equivalent weight in the range from about 300 to about
 2000, and from about 1% to about 20% by weight of one or
 more additives to adsorb moisture or carbon dioxide.

30 The polyamines or alkanolamines preferably have an
 equivalent weight in the range from about 30 to about 200
 and are present in an amount sufficient to form a coating
 which is substantially tack-free within about 5 minutes
 to about 60 minutes after being mixed with the
 isocyanate-containing component. In a specifically
 preferred embodiment, the polyamines or alkanolamines

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1 make up from about 2% to about 7% by weight of the
curative component and are diethyl toluenediamine.

5 The curative component can also include one or more catalysts to promote the hydroxyl-isocyanate reaction in formation of a polyurethane or poly(urea)urethane. Preferably the two components have an isocyanate to active hydrogen equivalent ratio of from about 0.85 to about 1.15. When the components are blended with a pigment and/or other additives or fillers the blend 10 preferably has an average equivalent weight of from about 150 to about 500. These optional pigments and/or other additives or filler are part of the curative component prior to blending.

15 The present invention also encompasses a method wherein the isocyanate-containing component and curative component are separately delivered to a manifold, preferably in a volumetric ration of 1:1. The components are then mixed with each other and sprayed through an atomizing nozzle onto a surface to produce a polyurethane 20 or poly(urea)urethane coating. For spraying the mixture at ambient temperatures, around 70°F to 100°F, the isocyanate-containing component and the curative component preferably have viscosities less than 1000 centipoise at these temperatures.

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Objects of the Invention

30 This invention provides solventless, polyurethane coating compositions which combine the ambient temperature ease of applying solventless, one-shot polyurethane coating systems with the lower moisture sensitivity and superior physical properties of the coatings produced from solventless, prepolymer-based polyurethane coating compositions.

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Preferably, the coating system of this invention includes Parts A and B which are mixed substantially 1:1

1 by volume.

5 Preferably, Part B (the curative component) comprises essentially a major portion of a blend of high molecular weight polyol or polyamine and low molecular weight glycol, a minor portion of a highly reactive alkanolamine or polyamine, and an additive to adsorb moisture and CO₂. Preferably, Part B also produces a thixotropic mixture approximately 30 seconds after being combined with the Part A (the isocyanate-containing component). This thixotropic mixture can be spray-applied to thicknesses of from 20-250 mils on vertical surfaces without sagging even though it is applied at ambient temperature, and it is tack-free in 5-60 minutes.

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15 In the preferred spraying method of this invention, the Part A and Part B components are pumped from separate containers into a manifold where they are mixed 1:1 by volume, and then delivered through a single "whip-hose" to a spray nozzle for application to the surface to be coated.

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1 Detailed Description of the Invention

5 This invention provides two-component, solventless polyurethane compositions which may be combined at substantially 1:1 by volume, and applied with commercially available, plural component, airless-spray equipment at ambient temperatures.

10 The Part A, or isocyanate-containing component, includes a liquid polyisocyanate, polyisocyanurate, or isocyanate-terminated prepolymer or quasi-prepolymer with a reactive isocyanate content of from about 12-25% by weight. Quasi-prepolymers useful in this invention are materials made by reacting a polyurethane forming polyol or polyamine with an excess of a polyurethane forming aliphatic or aromatic polyisocyanate such as poly-15 methylene polyphenyl isocyanate, 4,4'-diphenylmethane diisocyanate (MDI), and liquid carbodiimide or uretonimine modified MDI variants. Other useful isocyanates include: 3-isocyanatomethyl-3,5,5,-trimethylcyclohexyl isocyanate (IPDI); bis (4-isocyanatocyclohexyl) methane (Desmodur W); xylene diisocyanate (XDI); m-and-p-tetramethyl xylene diisocyanate (m-and-p-TXMDI); "dimeryl" diisocyanate (DDI); and adducts or trimers of hexamethylene diisocyanate with free monomeric isocyanate content less than 0.7% such as Desmodur N3200 and N3300. Toluene diisocyanate (TDI) adducts with free monomeric TDI content of less than 0.7% may also be employed.

20 The polyol or polyamines used to make the quasi-prepolymer are poly(alkylene ether) glycols, polyester glycols, polycaprolactone glycols, polycarbonate glycols, castor oils, polybutadiene glycols, polyether-thioether-glycols and the like of which the following are mentioned as non-limiting examples:

30 35 polytetramethylene ether glycols, MW 650-2900

- 1 polypropylene ether glycols, MW 400-4000
castor oil and castor oil derivatives, MW 300-1000
polycaprolactone glycols, MW 300-2000
polydiethylene adipate, MW 500-2000
5 hydroxyl-terminated Bisphenol A polyols, MW 400-1000
polycarbonate glycols, MW 500-2500
polybutylene and ethylene/butylene adipate, MW 500-2000
polyetherthioether glycols, MW 400-2000
10 hydroxyl functional acrylic polyols, MW 300-1000
The second component of the present invention is a Part B or curative component which is preferably comprised of:
(a) 0 to 15% by weight of a polyamine (di-or-polyamine) or an alkanolamine with an equivalent weight of 30 to 200;
(b) 10 to 20% by weight of a glycol having an equivalent weight of from 30 to 200;
(c) 40 to 80% by weight of a high molecular weight polyol or polyamine with equivalent weight of from 300-2000; and
20 (d) 1 to 20% by weight of an additive to adsorb moisture or CO₂.
These are blended to have an average equivalent weight of from 150 to 500.
25 The curative component may also contain pigments or dyes, rheological additives, surfactants, UV stabilizers, and fillers such as silica or silica flour, barytes, talc, aluminum trihydrate, calcium carbonate and the like. Catalysts which promote the hydroxyl-isocyanate reaction in formation of a polyurethane are highly desirable constituents of the curative component. Catalysts well known in the art include such materials as dibutyltin dilaurate, stannous octoate, lead octoate, phenylmercuric propionate, ferric acetylacetone and
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1 organo-zinc compounds such as zinc octoate. The
preferred catalyst is the composition Cotin 222 sold by
Cosan Chemical Corporation. Cotin 222 is an organo-tin
5 carboxylate containing negligible free acid and is
described in detail in U.S. Patent No. 3,661,887, which
is incorporated herein by reference. Coscat 83, a
proprietary organo-metallic composition based on bismuth
and sold by Cosan Chemical Corp., can also be used.
Catalysts are particularly desirable when the
10 polyurethane coatings are applied in the presence of
moisture. The catalyst promotes the hydroxyl-isocyanate
reaction in favor of the reaction of isocyanate with
water so that the superior physical properties of the
coating are maintained.

15 Catalysts also act to accelerate the cure time of
the coating and allow application to vertical surfaces
without sagging. In fact, if enough catalyst is added to
the curative component of this invention, the percent by
weight of polyamine or alkanolamine used in the curative
20 component can be reduced to zero. However, this does not
result in the most preferable coating because the
physical properties of the coating suffer somewhat when
the percent by weight of polyamine or alkanolamine is
reduced below two.

25 The following are non-limiting illustrative examples
of essential constituents of the curative or Part B
component:

30 Polyamines or alkanolamines with equivalent weight
of 30 to 200 include triethanolamine, 1,6-hexanediamine,
Quadrol (BASF), methylene dianiline, menthanediamine,
isophorone diamine, 1,4-diamino cyclohexane, Lauramin
C-260 (BASF), PACM-20 (Dupont), Jeffamine T400 (Texaco),
methylene-bis-2,6 diisopropylaniline ("MDPA": from Ethyl
or "MDIPA": from Lonza), diethyl toluenediamine (DETDA
35 sold by Ethyl and Lonza), t-butylbenzenediamine,

1 methylene-bis-2,-diethylaniline, 2,2-diaminodiphenyl
disulphide, 1,3-propanediol di-p-aminobenzoate, bis
(2-aminophenylthio) ethane, and methylene bis
5 N-methylanthranilate. The type of polyamine or
alkanolamine selected depends on the
isocyanate-containing component used to form the
polyurethane. If the isocyanate component is based on
10 aliphatic isocyanate, a very reactive aliphatic or
cyloaliphatic polyamine such as 1,6-hexanediamine,
PACM-20 sold by Dupont, isophorone diamine or
menthanediamine is used. If the isocyanate component is
15 based on aromatic diisocyanate, aromatic diamines such as
methylenedianiline, and diethyltoluenediamine may be
used. The specific amount, if any, of polyamine used
reacts to form a thixotropic mixture approximately 15
20 seconds to 2 minutes after mixing with the isocyanate
containing component, preferably this amount ranges from
25 2 to 7% by weight of the curative component.

20 The second preferred constituent of the curative
component is a glycol or polyol having an equivalent
weight of from 30 to 200. Useful glycols include
ethylene glycol, trimethylolpropane, 1,3-butylene glycol,
1,4-butylene glycol, 2,ethyl-1,3-hexanediol,
1,5-pentanediol, 1,6-hexanediol, dipropylene glycol,
25 glycerol, neopentylglycol, thiodiglycol, bisphenol A-and
bisphenol F-based glycols, dihydroxyethylethers of
resorcinol and hydroquinone, and low molecular weight
polyalkylene ether glycols. The presence of the glycol
30 in the curative component helps contribute to the low
temperature sprayability of the spray composition.

30 The third preferred constituent of the curative
component is a relatively high molecular weight polyol or
polyamine having an equivalent weight of from 300-2000.
Particularly useful polyols are polytetramethylene ether
35 glycol, poly(ethylene oxide)-terminated polypropylene

1 ether glycols, castor oil, polypropylene ether glycols,
polyethylene-butylene adipate glycols, polybutadiene
glycols, polyetherthioether glycols and oligomeric
diaminobenzoates such as Polyamine-1000 sold by Polaroid.

5 The fourth preferred constituent of the curative
component is a non-reactive additive which reduces
blistering and blowing or foaming during application of
the solventless polyurethane coating system in humid
weather or on damp substrates by combining with or
10 adsorbing moisture and/or carbon dioxide. Suitable
moisture scavenging additives are calcium sulfate,
calcium oxide and synthetic zeolite "molecular sieves".
The amount of moisture scavenging additive used is
increased according to the expected humidity at the point
15 where the coating is to be applied.

15 Preferably, the low molecular weight polyamine, low
molecular weight glycol, high molecular weight polyol,
and moisture-adsorbing additive are blended with pigment,
catalyst and other additives in Part B (curative) to an
20 average equivalent weight of from 150 to 500. The
equivalent weight of the curative blend depends on the
isocyanate content of the Part A or isocyanate containing
component, and is calculated to give an isocyanate to
active hydrogen equivalent ratio of from 0.85 to 1.15
25 based on a 1:1 volumetric mixture of Part A to Part B.

25 The isocyanate and curative components typically
have viscosities of less than 1000 centipoise at 70°F and
are pumped directly from drums in two separate 3000 psi,
1/4 inch ID paint hoses to 1:1 proportioning cylinders
30 mounted below a 30:1, air-regulated Graco Bulldog pump
which delivers equal volumes of both components to a
manifold fitted with static mixer. The components are
thoroughly mixed as they pass through the manifold and
static mixer into a single, 3/16 inch ID "whip-hose" and
are delivered to a standard, airless spray gun such as a

1 Graco Silver. The mixed components have sufficient
potlife to permit the use of 25 to 50 feet of whiphose
and "triggering" of the spray gun to the off position for
30-45 seconds. The whiphose and standard airless spray
5 gun is less cumbersome than the three hoses and
plural-component, internal-mix spray gun used to spray
prepolymer-based polyurethane coating systems, and is
easier to use in confined or restricted-access areas.
Triggering of the spray gun off during the coating
10 operation often results in less overspray and more
economical use of material as the gun is moved from a
sprayed area to a non-sprayed area.

15 The mixed composition is atomized at the spray gun
tip and deposited on the surface to be coated at
thicknesses of from 15 to 30 mils per pass. The
thixotropic mixture permits multiple passes of the spray
gun and continuous film build up to 250 mils without
sagging. The applied coating is tack-free in from 5 to
20 60 minutes and is ready for service within 4 to 24 hours,
depending on the application.

25 The coating compositions of the present invention
exhibit excellent adhesion by themselves to many
substrates including metal, wood and concrete. A primer
or adhesive is not required for many applications, if the
substrate has been properly prepared and cleaned.
Coating compositions of the present invention exhibit
30 excellent adhesion to ferrous metal substrates which have
been sandblasted to a near-white metal finish
(SSPC-SP-10) with 2-3 mil profile and concrete that has
been sweepblasted or acid-etched. When there is a long
period of time between blasting the metal and coating or
where optimum adhesion and corrosion protection are
desired, primers such as Amerthane^R 135, Amercoat^R 2183,
Amercoat^R 460, Amercoat^R 66, and Amerlock^R 400 should be
used. Concrete with rough surfaces or cracks may be
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1 filled with a cementitious coating such as Nu-Klad^R 965
or an epoxy-surfacer such as Nu-Klad^R 114 and then sealed
with a primer such as Amerthane^R 135.

5 The solventless polyurethane compositions of this
invention form polyurethane coatings useful in many
applications. The isocyanate and curative components are
selected for a particular application based on the
physical characteristics and chemical resistance
characteristics of the polyurethane they produce. For
example, coating systems based on polytetramethylene
ether glycol are well suited for applications which
require good resistance to abrasive wear such as
ore-handling equipment, and hopper cars. Coating systems
based on castor oil provide good hydrolytic stability and
chemical resistance, such as for wastewater treatment
15 ponds and chemical or crude oil storage tanks.

20 The spray system of this invention has major
advantages compared to high-solids, solvent-containing
polyurethane coating systems; solventless, one shot
polyurethane coating systems; and prior-art solventless,
prepolymer-based polyurethane coating systems.

The major advantages compared to solvent-containing
systems are:

1. There are no volatile solvents which present health
25 or explosion hazards, and there are no limitations
arising from environmental regulations on volatile
organic compound emissions.
2. The spray system of the present invention can, with
multiple passes, apply high coating thicknesses of
30 from 20 to 250 mils without sagging compared to 10
to 40 mils for solvent-containing systems.
3. Tack-free time and curing are short, which allows
for quick recoating and reduces the time required
for the applied coating to be handled or placed in
service.

- 1 4. The solventless system of the present invention requires less volume to apply the same dry film thickness than a solvent-containing system; there is less material to store, handle, and apply.
- 5 5. Problems associated with solvent-containing systems such as shrinkage, blistering, holidays and premature deadhesion caused by solvent retained in the applied coating are significantly reduced.

10 The major advantages of the present invention compared to solventless, one-shot, polyurethane coating systems are reduced sensitivity to moisture-generated foaming, and improved physical properties such as higher tensile and tear strength.

15 Spray compositions of the present invention have equivalent physical properties such as tensile and tear strength compared to prior-art, solventless, prepolymer-based polyurethane systems but have the following major advantages:

- 20 1. Spray compositions of the present invention are low viscosity liquids that can be applied at 70°F - 100°F. The need for expensive, additional equipment required to preheat, maintain and apply prepolymer-based coating systems is eliminated.
- 25 2. Coating systems of the present invention are applied with a single paint hose and standard, airless spray gun, which is easier to use than the internal-mix, plural-component guns used to apply prior-art, prepolymer-based coating systems.
- 30 3. The compositions of the present invention have sufficient pot-life to allow triggering of the spray gun for 30-45 seconds, which reduces overspray and consumes less material when coating complicated shapes.
- 35 4. The components of the present invention are combined 1:1 by volume, which is desirable for optimum

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1 mixing, and is more forgiving to off-ratio conditions which frequently occur during field application using plural component, airless spray equipment.

5 5. Despite being applied at 70°F - 100°F and requiring 5 to 60 minutes for the coating to be tack-free, a continuous film of up to 250 mils in thickness can be applied without sagging so that spray compositions of the present invention have equivalent physical properties compared to prior-art, solventless, prepolymer-based polyurethane systems applied at higher temperatures and having faster cure times.

10 The following examples illustrate, but do not limit, the present invention.

15

EXAMPLE I

Preparation of An MDI/polypropylene Ether Glycol

Quasi-Prepolymer (Part A)

20 7505.0 grams (52.3 eqs) of carbodiimide modified MDI, Isonate 143L sold by Upjohn, was charged to a resin flask equipped with an agitator, thermometer, N₂ inlet, condenser, and an addition funnel. 2450.0 grams (4.9 eqs) of predried Niax Polyol PPG1025 (%H₂O content less than 0.05%) was charged to the addition funnel and added to the Isonate 143L with continuous agitation and nitrogen blanketing. The exotherm was kept below 50°C by adjusting the addition rate. After the addition of Niax Polyol PPG1025 was complete, the temperature was raised to 70°C and held for one hour. Table I shows the results.

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Preparation of the Curative Blend (Part B)

The constituents listed below were charged to a resin flask equipped as described in the prepolymer preparation.

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		Parts by Weight (grams)	<u>Equivalents</u>
1	<u>Ingredients</u>		
	Castor DB Oil, Caschem	4821.0	14.1
	2-ethyl-1,3 hexanediol	1474.0	20.2
	DETDA, Ethyl	636.0	7.1
5	Niax Polyol PPG 1025, Union Carbide	1373.0	2.8
	Baylith L Paste, Mobay	1264.0	1.8
	PDI 47055B, PDI Inc.	406.0	0.2
	Dibutyltindilaurate	3.0	---
10	The ingredients were heated at 100°C under vacuum until the moisture content was less than 0.08% by weight. Table I shows the results.		

EXAMPLE IIPreparation of An MDI/Polytetramethylene Ether Glycol15 Quasi-Prepolymer (Part A)

The same procedure used to prepare Part A in Example I was used except that the components were 11,125.0 grams (82.1 eqs) Rubinate XI-208 from Rubicon and 5105.0 grams (10.0 eqs) Terrathane 1000 from Dupont. Table I shows
20 the results.

Preparation of Curative Blend (Part B)

The same procedure used to prepare the Part B of Example I was used with the components listed below.

		Parts by Weight (grams)	<u>Equivalents</u>
25	<u>Ingredients</u>		
	Terrathane 1000, Dupont	964.8	1.890
	Voranol XAS1077.02, Dow	688.9	0.630
	1,4 butanediol	255.5	5.670
	DETDA, Ethyl	157.5	1.770
30	PDI 47055-B, PDI	86.5	0.035
	Coscat 83, Cosan	1.3	---
	Baylith L Powder, Mobay	38.8	---

The Part A and Part B from each example were combined 1:1 by volume and sprayed using the equipment previously described. Table I shows the results.

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TABLE I

1	<u>Part A</u>	<u>Example I</u>	<u>Example II</u>
	%NCO	19.7	18.7
	Visc @ 75°F, cP	600	900
5	<u>Part B</u>		
	%H ₂ O, KF	0.08	0.09
	Visc @ 75°F, cP	600	800

Physical Properties of Spray-Applied, 1:1 Volume Mix

10	<u>Aged 14 Days at 75°F/50% R.H.</u>		
	Hardness	60 Shore D	90 Shore A
	Tensile, psi	3500	3000
	Elongation, %	120	320
	Tear, DieC	500	400
15	Resilience, Bashore	30	27
	Abrasion Resistance, Wt. loss, mg. (H-10 Wheel/1000g/1000r)	50	40
	Elcometer Adhesion, psi (unprimed cold-rolled steel)	1800	1500
20	Numerous variations can be made in the practice of the invention, by selecting particular polyisocyanate, polyisocyanurate or isocyanate-terminated prepolymers or quasi-prepolymers and combinations thereof, and by selecting particular curative components comprised of particular polyamines or alkanolamines, particular glycols, particular high molecular weight polyols or polyamines, particular moisture-adsorbing additives, particular catalysts and any other desired additives or fillers, to establish the specific physical and chemical characteristics and economics of use appropriate for the surface to be coated.		
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1 I CLAIM:

1. A two-component solventless spray composition for producing polyurethane and poly(urea)urethane coatings comprised of substantially equal volumes of:

5 an isocyanate-containing component comprised of a liquid polyisocyanate, polyisocyanurate or isocyanate-terminated prepolymer or quasi-prepolymer; and

10 a curative component comprised of from about 0% to about 15% by weight of one or more polyamines or alkanolamines in an amount sufficient to react to form a thixotropic mixture about 15 seconds to about 2 minutes after being mixed with the isocyanate-containing component, from about 10% to about 20% by weight of one or more glycols having an equivalent weight in the range from about 30 to about 200, from about 40% to about 80% be weight of one or more high molecular weight polyols or polyamines having an equivalent weight in the range from about 300 to about 2000, and at least about 1% by weight of one or more additives to adsorb moisture or carbon dioxide.

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2. A composition as set forth in claim 1 wherein the polyamines or alkanolamines have an equivalent weight in the range from about 30 to about 200.

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3. A composition as set forth in claim 1 wherein the curative component is also comprised of one or more catalysts to promote the hydroxyl-isocyanate reaction in formation of a polyurethane or poly(urea)urethane.

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4. A composition as set forth in claim 1 wherein the additives to adsorb moisture are selected from the group consisting of calcium sulfate, calcium oxide or synthetic zeolite molecular sieves.

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1 5. A composition as set forth in claim 3 wherein the catalysts are selected from the group consisting of dibutyltin dilaurate, stannous octoate, lead octoate, phenylmercuric propionate, ferric acetylacetone, organo-tin carboxylates, organo-bismuth compounds or 5 organo-zinc compounds such as zinc octoate.

10 6. A composition as set forth in either of claims 1 or 3 wherein the components when blended have an average equivalent weight of from about 150 to about 500.

15 7. A composition as set forth in either of claims 1 or 2 wherein the components have an isocyanate to active hydrogen equivalent ratio of from about 0.85 to about 1.15.

20 8. A composition as set forth in claim 1 wherein each component has a viscosity less than 1000 centipoise at 70°F.

25 9. A composition as set forth in claim 1 wherein the one or more polyamines or alkanolamines make up from about 2% to about 7% by weight of the curative component.

30 10. A composition as set forth in claim 1 wherein the one or more polyamines or alkanolamines are diethyl toluediamine.

35 11. A composition as set forth in claim 1 wherein the isocyanate-containing component is based on aliphatic isocyanate and the polyamine or alkanolamine is a very reactive aliphatic or cyloaliphatic polyamine.

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1 12. A composition as set forth in claim 1 wherein the isocyanate-containing component is based on aromatic diisocyanate and the polyamine or alkanolamine is an aromatic diamine.

5 13. A composition as set forth in claim 1 wherein the one or more additives to adsorb moisture or carbon dioxide make up from about 1% to about 20% by weight of the curative component.

10 14. A two-component solventless spray composition for producing polyurethane and poly(urea)urethane coatings comprised of:

15 an isocyanate-containing component comprised of a liquid polyisocyanate, polyisocyanurate or isocyanate-terminated prepolymer or quasi-prepolymer; and

20 a curative component comprised of from about 0% to about 15% by weight of one or more polyamines or alkanolamines in an amount sufficient to form a coating which is substantially tack-free within about 5 minutes to about 60 minutes after being mixed with the isocyanate-containing component, from about 10% to about 20% by weight of one or more glycols having an equivalent weight in the range from about 30 to about 200, from about 40% to about 80% by weight of one or more high molecular weight polyols or polyamines having an equivalent weight in the range from about 300 to about 2000, and from about 1% to about 20% by weight of one or more additives to adsorb moisture or carbon dioxide.

25 15. A two-component solventless spray composition for producing polyurethane and poly(urea)urethane coatings comprised of:

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1 an isocyanate-containing component comprised of a
liquid polyisocyanate, polyisocyanurate or isocyanate-
terminated prepolymer or quasi-prepolymer; and

5 a curative component comprised of from about 2%
to about 7% by weight of one or more polyamines or
alkanolamines having an equivalent weight in the range
from about 30 to about 200, from about 10% to about 20%
by weight of one or more glycols having an equivalent
10 weight in the range from about 30 to about 200, from
about 40% to about 80% by weight of one or more high
molecular weight polyols or polyamines having an
equivalent weight in the range from about 300 to about
2000, and from about 1% to about 20% by weight of one or
more additives to adsorb moisture or carbon dioxide.

15 16. A method for the solventless spray application of
a polyurethane or poly(urea)urethane coating, comprising
the steps of:

20 delivering to a manifold an isocyanate-containing
component comprised of a liquid polyisocyanate,
polyisocyanurate or isocyanate-terminated prepolymer or
quasi-prepolymer;

25 delivering to said manifold a curative component
comprised of from about 0% to about 15% by weight of one
or more polyamines or alkanolamines having an equivalent
weight in the range from about 30 to about 200, from
about 10% to about 20% by weight of one or more glycols
having an equivalent weight in the range from about 30 to
about 200, from about 40% to about 80% by weight of one
30 or more high molecular weight polyols or polyamines
having an equivalent weight in the range from about 300
to about 2000, and from about 1% to about 20% by weight
of one or more additives to adsorb moisture or carbon
dioxide;

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1 mixing the isocyanate-containing component and
the curative component with each other; and

5 spraying the resulting mixture through an
atomizing nozzle onto a surface to produce a polyurethane
or poly(urea)urethane coating.

10 17. A method as set forth in claim 16 wherein the
isocyanate-containing component and the curative
component are delivered to the manifold in a volumetric
ratio of 1:1.

15 18. A method as set forth in claim 16 wherein the
average equivalent weight of the resulting mixture is in
the range of from about 150 to about 500.

19. A method as set forth in claim 16 wherein the
isocyanate-containing component and the curative
component each have viscosities less than 1000 centipoise
at ambient temperatures.

20 20. A method as set forth in claim 16 wherein the one
or more additives to adsorb moisture or carbon dioxide
make up from about 2% to about 8% by weight of the
curative component.

25 21. The product of any of the methods set forth in
claims 14-20 inclusive.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/01216

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4); C08L 75/04

U.S. CL. 528/55

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
U.S.	528/55, 56, 57, 58, 60, 61, 64, 65, 66, 75, 76, 77

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁰ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 4,257,299 (OECHSLE) 12 MAY 1981	1-21
A	US, A, 4,195,148 (HAGEN) 25 MARCH 1980	1-21
A	US, A, 4,234,445 (HAGEN) 18 NOVEMBER 1980	1-21

* Special categories of cited documents: ¹⁶

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the Invention

"X" document of particular relevance; the claimed Invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed Invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ²

19 AUGUST 1987

Date of Mailing of this International Search Report ²

08 SEP 1987

International Searching Authority ¹

ISA/US

Signature of Authorized Officer ²⁰

M. J. WELSH 